

### **"Use of Lubricants Based on Polysiloxanes"**

This invention relates to the use of polysiloxane-containing lubricant formulations. The invention also relates to lubricants containing polysiloxanes and other additives.

5 In the food industry and especially in beverage factories, the  
containers to be filled in the bottling plants are conveyed by conveyors  
differing in design and constituent materials, for example by platform  
conveyors or chain-like arrangements which are generally referred to  
hereinafter as chain conveyors. The conveyors establish the connection  
10 between the various optional treatment stages of the bottling process such  
as, for example, the unpacker, bottle washer, filler, closer, labeller, packer,  
etc. The containers may assume various forms, more particularly glass  
and plastic bottles, cans, glasses, casks, beverage containers (kegs),  
paper and paperboard containers. To guarantee uninterrupted operation,  
the conveyor chains have to be suitably lubricated to avoid excessive  
15 friction with the containers. Dilute aqueous solutions containing suitable  
friction-reducing ingredients are normally used for lubrication. The chain  
conveyors are contacted with the aqueous solutions by dipping or spraying,  
for example, the corresponding lubrication systems being known as dip  
lubrication or automatic belt lubrication or central chain lubrication systems.

20 The chain lubricants hitherto used as lubricants are mostly based on  
fatty acids in the form of their water-soluble alkali metal or alkanolamine  
salts or on fatty amines, preferably in the form of their organic or inorganic  
salts.

Whereas both classes of substances can be used without difficulty in  
25 dip lubrication, they are attended by a number of disadvantages in the  
central chain lubrication systems typically in use today. Thus, **DE-A-23 13**

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**330** describes soap-based lubricants containing aqueous mixtures of C<sub>16-18</sub> fatty acid salts and surface-active substances. Soap-based lubricants such as these have the following disadvantages:

1. They react with the hardness ions in water, i.e. the alkaline earth metal ions, and other ingredients of water to form poorly soluble metal soaps, so-called primary alkaline earth metal soaps.
2. A reaction takes place between the soap-based lubricants and carbon dioxide dissolved in water or in the product to be bottled.
3. The in-use solution thus prepared is always germ-promoting.
4. Where hard water is used, ion exchangers have to be employed to soften the water which means an additional source of germs (and is therefore hardly encountered in practice) or, alternatively, products of high complexing agent content have to be used which is ecologically unsafe.
5. Increased foaming occurs which can cause problems in particular at the bottle inspector (automatic bottle control) and results in greater wetting of the transport containers.
6. Most of these products contain solvents.
7. The cleaning effect of the products is poor so that separate cleaning is necessary.
8. Corresponding soap-based lubricant preparations show pH-dependent performance.
9. In addition, soap-based lubricant preparations are dependent on the water temperature.
10. Soap-based lubricants show poor stability in storage, particularly at low temperatures.
11. The EDTA (ethylenediamine tetraacetate) present in many products is known to have poor biodegradability.
12. Soap-based lubricant preparations are not suitable for all plastic transport containers because, in many cases, they give rise to stress

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cracking in the transport container.

Besides soap-based lubricants, lubricants based on fatty amines are mainly used. Thus, **DE-A-36 31 953** describes a process for lubricating chain-type bottle conveyors in bottling factories, more particularly in breweries, and for cleaning the conveyors with a liquid cleaning composition, characterized in that the chain-type bottle conveyors are lubricated with belt lubricants based on neutralized primary fatty amines which preferably contain 12 to 18 carbon atoms and which have an unsaturated component of more than 10%.

**EP-A-0 372 628** discloses fatty amine derivatives corresponding to the following formulae:



in which

$\text{R}^1$  is a saturated or unsaturated, branched or linear alkyl group containing 8 to 22 carbon atoms,

$\text{R}^2$  is hydrogen, an alkyl or hydroxyalkyl group containing 1 to 4 carbon atoms or  $\text{-A-NH}_2$ ,

$\text{A}$  is a linear or branched alkylene group containing 1 to 8 carbon atoms

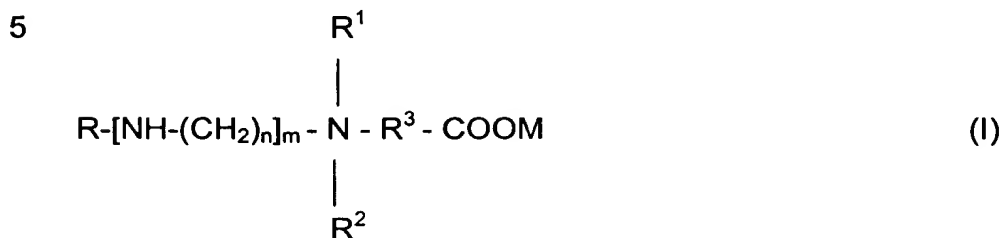
and

$\text{A}^1$  is a linear or branched alkylene group containing 2 to 4 carbon atoms, as lubricants.

In addition, lubricants based on N-alkylated fatty amine derivatives which contain at least one secondary and/or tertiary amine are known from **DE-A-39 05 548**.

**DE-A-42 06 506** relates to soapless lubricants based on amphoteric

compounds, primary, secondary and/or tertiary amines and/or salts of such amines corresponding to general formulae (I), (IIa), (IIb), (IIIa), (IIIb), (IIIc), (IVa) and (IVb):



in which

R is a saturated or mono- or polyunsaturated, linear or branched alkyl group containing 6 to 22 carbon atoms which may optionally be substituted by -OH, -NH<sub>2</sub>, -NH-, -CO-, -(CH<sub>2</sub>CH<sub>2</sub>O)<sub>i</sub>- or -(CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>O)<sub>i</sub>-;

R<sup>1</sup> is hydrogen, an alkyl group containing 1 to 4 carbon atoms, a hydroxy-alkyl group containing 1 to 4 carbon atoms or a group -R<sup>3</sup>COOM,

R<sup>2</sup> is hydrogen, an alkyl group containing 1 to 4 carbon atoms or a hydroxyalkyl group containing 1 to 4 carbon atoms, but only where M represents a negative charge,

R<sup>3</sup> is a saturated or mono- or polyunsaturated, linear or branched alkyl group containing 1 to 12 carbon atoms which may optionally be substituted

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tuted by -OH, -NH<sub>2</sub>, -NH-, -CO-, -(CH<sub>2</sub>CH<sub>2</sub>O)<sub>l</sub>- or -(CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>O)<sub>l</sub>-,

R<sup>4</sup> is a substituted or unsubstituted, linear or branched, saturated or mono- or polyunsaturated alkyl group containing 6 to 22 carbon atoms which may contain at least one amine, imine, hydroxy, halogen and/or carboxy group as substituent, a substituted or unsubstituted phenyl group which may contain at least one amine, imine, hydroxy, halogen, carboxy and/or a linear or branched, saturated or mono- or polyunsaturated alkyl group containing 6 to 22 carbon atoms as substituent,

R<sup>5</sup> is hydrogen or - independently of R<sup>4</sup> - has the same meaning as R<sup>4</sup>,

X<sup>-</sup> is an anion from the group consisting of amidosulfonate, nitrate, halide, sulfate, hydrogen carbonate, carbonate, phosphate or R<sup>6</sup>-COO<sup>-</sup> where

R<sup>6</sup> is hydrogen, a substituted or unsubstituted, linear or branched alkyl group containing 1 to 20 carbon atoms or alkenyl group containing 2 to 20 carbon atoms, which may contain at least one hydroxy, amine or imine group as substituent, or a substituted or unsubstituted phenyl group which may contain an alkyl group with 1 to 20 carbon atoms as substituent, and

R<sup>7</sup> and R<sup>8</sup> independently of one another represent a substituted or unsubstituted, linear or branched alkyl group containing 1 to 20 carbon atoms or alkenyl group containing 2 to 20 carbon atoms which may contain at least one hydroxy, amine or imine group as substituent, or a substituted or unsubstituted phenyl group which may contain an alkyl group with 1 to 20 carbon atoms as substituent,

M is hydrogen, alkali metal, ammonium, an alkyl group containing 1 to 4 carbon atoms, a benzyl group or a negative charge,

n is an integer of 1 to 12,

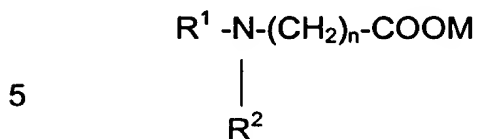
m is an integer of 0 to 5 and

l is a number of 0 to 5,

containing alkyl dimethylamine oxides and/or alkyl oligoglycosides as nonionic surfactants.

**EP-B-629 234** discloses a lubricant combination consisting of

a) one or more compounds corresponding to the following formula:



in which

$\text{R}^1$  is a saturated or mono- or polyunsaturated, linear or branched alkyl group containing 6 to 22 carbon atoms which may optionally be substituted by -OH, -NH<sub>2</sub>-, -NH-, -CO-, halogen or a carboxyl group,

$\text{R}^2$  is a carboxyl group containing 2 to 7 carbon atoms,

M is hydrogen, alkali metal, ammonium, an alkyl group containing 1 to 4 carbon atoms or a benzyl group and

n is an integer of 1 to 6,

b) at least one organic carboxylic acid selected from monobasic or polybasic, saturated or mono- or polyunsaturated carboxylic acids containing 2 to 22 carbon atoms,

c) optionally water and additives and/or auxiliaries.

**WO 94/03562** describes a lubricant concentrate based on fatty amines and optionally typical diluents or auxiliaries and additives, characterized in that it contains at least one polyamine derivative of a fatty amine and/or a salt of such an amine, the percentage content of the polyamine derivatives of fatty amines in the formulation as a whole being from 1 to 100% by weight.

In one preferred embodiment of **WO 94/03562**, this lubricant concentrate contains at least one polyamine derivative of a fatty amine corresponding to the following general formula:



in which

R is a substituted or unsubstituted, linear or branched, saturated or mono- or polyunsaturated alkyl group containing 6 to 22 carbon atoms, the substituents being selected from amino, imino, hydroxy, halogen and carboxy, or a substituted or unsubstituted phenyl group, the substituents being selected from amino, imino, hydroxy, halogen, carboxy and a linear or branched, saturated or mono- or polyunsaturated alkyl group containing 6 to 22 carbon atoms,

A represents either -NH- or -O-,

X<sup>-</sup> is an anion of an inorganic or organic acid,

k, l and m independently of one another are integers of 1 to 6,

y is 0, 1, 2 or 3 where A = -NH- or 1, 2, 3 or 4 where A = -O- and

n is an integer of 0 to 6.

The problem addressed by the present invention was to enable conveyor belt installations to be lubricated with silicone-containing formulations, to further reduce water consumption and to achieve high material compatibility with plastic containers.

The present invention relates to the use of formulations containing at least 1% by weight and preferably at least 5% by weight, based on the formulation as a whole, of at least one polysiloxane preferably selected from the groups of linear, branched, cyclic and crosslinked polysiloxanes for lubricating conveyor belt installations in the food industry, the formulations being applied to the conveyor belt installations directly, i.e. without dilution with water in the food factory, via an application system which is preferably in direct contact with the surfaces to be lubricated during application or which, in another preferred embodiment, is in the form of a spray applicator. In one preferred use according to the invention, the formulations additionally contain at least one component selected from fluorine and polyhydroxy compounds and/or ethers and esters thereof.

Where fluorine compounds are used in the formulations to be used

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- a) perfluorinated or partly fluorinated monomeric organic compounds,
- b) pure and mixed dimers and oligomers based on at least one perfluorinated or partly fluorinated organic monomer,
- c) pure and mixed polymers based on at least one perfluorinated or partly fluorinated organic monomer.

According to the invention, the definition of the boundary between oligomers and polymers is based on the generally known characterization of polymers which are made up of so many identical or similar low molecular weight units (monomers) that the physical properties of these substances, particularly their viscoelasticity, do not change significantly when the number of units is increased or reduced by one unit. This is generally the case when the average molecular weight of the "polymers" is 10,000 g/mole or more.

The term oligomers is used for the low molecular weight dimers, trimers and other lower members of the polymer-homolog series.

In one preferred embodiment, the fluorine compounds a) comprise at least perfluorinated and partly fluorinated surfactants, alkanes, ethers and amines, the formulations used in accordance with the invention in one particularly preferred embodiment containing ammonium perfluoroalkyl sulfonates, lithium perfluoroalkyl sulfonates, potassium perfluoroalkyl sulfonates, amine perfluoroalkyl sulfonates, sodium perfluoroalkyl sulfonates, potassium fluoroalkyl carboxylates, quaternary fluorinated alkyl ammonium iodides, ammonium perfluoroalkyl carboxylates, fluorinated alkyl polyoxyethylene ethanols, fluorinated alkyl alkoxyates, fluorinated alkyl esters in concentrations of 0.001 to 10%. The fluorinated components of group c) are preferably perfluorinated and/or partly fluorinated alkoxy polymers which, in one particularly preferred embodiment, are obtainable from the copolymerization of tetrafluoroethylene and perfluoroalkoxyvinyl



ethers.

In another preferred embodiment, the formulations to be used in accordance with the invention contain at least perfluorinated and/or partly fluorinated polyethers from group c).

- 5       Where polyhydroxy compounds are used in the formulations to be used in accordance with the invention, they are preferably selected from the groups of polyalcohols and carbohydrates and, in one particularly preferred embodiment, from polyhydric alcohols, preferably alkanediols, alkanetriols and most preferably glycerol and the polyethers derived  
10       therefrom and also glucose, arabinose, ribulose, fructose and the oligo- and/or polysaccharides derived therefrom and esters and ethers thereof.

In another preferred embodiment, the formulations to be used in accordance with the invention are present in the form of one-component liquids, solutions, gels, emulsions, pastes, dispersions.

- 15       In one preferred embodiment, the formulations to be used in accordance with the invention additionally contain at least one antimicrobial component selected from the groups of alcohols, aldehydes, antimicrobial acids, carboxylic acid esters, acid amides, phenols, phenol derivatives, diphenyls, diphenyl alkanes, urea derivatives, oxygen and nitrogen acetals  
20       and formals, benzamidines, isothiazolines, phthalimide derivatives, pyridine derivatives, antimicrobial surface-active compounds, guanidines, antimicrobial amphoteric compounds, quinolines, 1,2-dibromo-2,4-dicyanobutane, iodo-2-propynyl butyl carbamate, iodine, iodophors, peroxides, the formulations to be used in accordance with the invention in one particularly  
25       preferred embodiment containing one or more compounds selected from ethanol, n-propanol, i-propanol, butane-1,3-diol, phenoxyethanol, 1,2-propylene glycol, glycerol, undecylenic acid, citric acid, 2-benzyl-4-chlorophenol, 2,2'-methylene-bis-(6-bromo-4-chlorophenol), 2,4,4'-trichloro-2'-hydroxydiphenyl ether, N-(4-chlorophenyl)-N-(3,4-dichlorophenyl)-urea,  
30       N,N'-(1,10-decanediyl-di-1-pyridinyl-4-ylidene)-bis-(1-octaneamine)-dihydro-

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chloride, N,N'-bis-(4-chlorophenyl)-3,12-diimino-2,4,11,13-tetraazatetradecane diimidoamide, quaternary ammonium compounds or alkyl amines, guanidines, amphoteric surfactants as antimicrobial components.

In another preferred embodiment, the formulations to be used in accordance with the invention contain other components selected from the groups of surfactants and solubilizing agents, at least one alkyl polyglycoside being present as surfactant in a particularly preferred embodiment. Other preferred constituents are fatty alkylamines and/or alkoxylates thereof, more particularly cocofatty amine ethoxylates, and/or imidazoline compounds and/or amphoteric surfactants and/or nonionic surfactants and/or ether carboxylic acids and/or ether amine compounds. In another preferred embodiment, paraffin compounds are added to the formulations to be used in accordance with the invention.

In practice, the formulations to be used in accordance with the invention are applied to the chain conveyors. In the most favorable case, the transport of the containers on the conveyors is not accompanied by foaming. By comparison with conventional lubricants which are diluted with water by a factor of more than 100 in automatic conveyor installations, the formulations to be used in accordance with the invention reduce frictional resistance between the conveyor and the containers transported thereon by more than 20% by for the same quantities by weight of active lubricating components applied to the conveyor installation over a certain period of time. This is demonstrated by the following Examples.

#### Example 1

A comparison formulation 1 which contains 5% by weight of coconut propylenediamine and which is adjusted to pH 7 with acetic acid is applied to the chain conveyors in a concentration in water of 0.2% through a nozzle block comprising five nozzles each capable of spraying 5 liters per hour. 50 ml of the comparison formulation or ca. 2.5 g of the coconut

propylenediamine are thus applied to the conveyor chains over a period of 1 hour. This test is carried out for 10 hours. According to the invention, the coefficient of friction between the bottles and the stainless steel conveyor chains is defined as the ratio of the tractive weight applied, for example, to a spring balance when an attempt is made to hold a bottle still while the conveyor is moving to the weight of that bottle.

Where the Comparison Example described above is used, the coefficient of friction  $\mu$  is 0.10. When spraying is stopped, the friction coefficient increases rapidly and the bottles fall over after only a few minutes.

In the Comparison Example, a total of 25 ml of lubricating coconut propylenediamine raw materials is applied to the conveyor chains over the total test duration of 10 hours. In a second test, 25 ml of a formulation to be used in accordance with the invention consisting of a 35% aqueous polydimethyl siloxane dispersion is distributed over the chain conveyors with a cloth. The coefficient of friction between the bottles and the chain conveyor is then measured over a period of 10 hours under exactly the same conditions as in Comparison Example 1. The coefficient of friction  $\mu$  is about 0.05 over the entire test duration of 10 hours. This Example shows that the friction coefficient between the bottles and the conveyor system can be reduced by more than 20% and, in the present case, even by more than 40%.

Another preferred embodiment of the present invention is the use of the formulations to be used in accordance with the invention for the conveying of plastic containers, the plastic containers in one particularly preferred embodiment containing at least one polymer selected from the groups of polyethylene terephthalates (PET), polyethylene naphthenates (PEN), polycarbonates (PC), PVC. In one most particularly preferred embodiment, the containers are PET bottles.

### Example 2

In a laboratory test, the stress cracking of a Comparison Example based on 5% by weight coconut propylene diamine and 5% by weight dimethyl lauryl amine adjusted to pH 7 with acetic acid is measured by comparison with the stress cracking of a 25% aqueous polydimethyl siloxane dispersion.

According to the test specification, PET bottles are filled with water and conditioned with carbon dioxide in such a way that a pressure of about 7 bar is present inside the bottles. The base cups of the bottles are then  
10 dipped in the formulation of the Comparison Example and the Example to be used in accordance with the invention and are placed in a Petri dish for 24 hours. Thereafter the bottles are opened, emptied and their base cups are rinsed with water. Visual inspection of the base cups of the bottles shows that, in the test with the Comparison Example, many stress cracks  
15 of average depth (classification C) are present whereas the test with the Example to be used in accordance with the invention produces only a few stress cracks of minimal depth (classification A). The stress cracks are classified in accordance with the reference images appearing in Chapter IV-22 of the book entitled **"CODE OF PRACTICE - Guidelines for an  
20 Industrial Code of Practice for Refillable PET Bottles", Edition 1, 1993-1994.**

Example 2 shows that the formulations to be used in accordance with the invention have advantages over typical commercial amine-based products used as lubricants in the conveying of plastic bottles.

25 In another preferred embodiment, the formulations to be used in accordance with the invention are used for conveying paperboard packs.

In another preferred use, the conveying surfaces of the conveyor belts are made of plastic - in one particularly preferred embodiment of polyacetal and polyethylene.

30 In another preferred embodiment, the conveying surfaces of the

conveyor belt are made of metal - in one particularly preferred embodiment stainless steel.

In another preferred embodiment, additional antimicrobial agents, more particularly organic peracids, chlorine dioxide or ozone, are additionally incorporated in the formulations to be used in accordance with the invention through separate feed systems either before or after application of the formulations.

In another preferred embodiment, the formulations to be used in accordance with the invention are applied to the conveyor belts without dilution with water using an aid selected from paint brushes, sponges, rollers, cloths, brushes, wipers, rubber, spray nozzles. In another preferred embodiment, the formulations to be used in accordance with the invention are diluted with water in automatic conveyor systems and the resulting solution is applied to the conveyors through metering systems, the dilution factor being between 10,000 and 100. In another preferred embodiment, the formulations to be used in accordance with the invention are selected and applied in such a way that there is no further proliferation of microorganisms on surfaces in contact with the formulations or solution. In one most particularly preferred embodiment, the number of microorganisms is reduced.

The present invention also relates to chain lubricants which, based on the formulation as a whole, contain at least 1% by weight and preferably at least 5% by weight of at least one polysiloxane and, in addition, at least one polyhydroxy compound and/or an organic fluorine compound, the sum total of polysiloxane and polyhydroxy compound and/or organic fluorine compound making up at least 15% by weight of the formulation as a whole in one preferred embodiment.

Where fluorine compounds are used in the formulations to be used in accordance with the invention, they are preferably selected from the groups of

- a) perfluorinated or partly fluorinated monomeric organic compounds,  
b) pure and mixed dimers and oligomers based on at least one perfluorinated or partly fluorinated organic monomer,  
c) pure and mixed polymers based on at least one perfluorinated or partly fluorinated organic monomer.

According to the invention, the definition of the boundary between oligomers and polymers is based on the generally known characterization of polymers which are made up of so many identical or similar low molecular weight units (monomers) that the physical properties of these substances, particularly their viscoelasticity, do not change significantly when the number of units is increased or reduced by one unit. This is generally the case when the average molecular weight of the "polymers" is 10,000 g/mole or more.

The term oligomers is used for the low molecular weight dimers, trimers and other lower members of the polymer-homolog series.

In one preferred embodiment, the fluorine compounds a) comprise at least perfluorinated and partly fluorinated surfactants, alkanes, ethers and amines, the formulations used in accordance with the invention in one particularly preferred embodiment containing ammonium perfluoroalkyl sulfonates, lithium perfluoroalkyl sulfonates, potassium perfluoroalkyl sulfonates, amine perfluoroalkyl sulfonates, sodium perfluoroalkyl sulfonates, potassium fluoroalkyl carboxylates, quaternary fluorinated alkyl ammonium iodides, ammonium perfluoroalkyl carboxylates, fluorinated alkyl polyoxyethylene ethanols, fluorinated alkyl alkoxyates, fluorinated alkyl esters in concentrations of 0.001 to 10%. The fluorinated components of group c) are preferably perfluorinated and/or partly fluorinated alkoxy polymers which, in one particularly preferred embodiment, are obtainable from the copolymerization of tetrafluoroethylene and perfluoroalkoxyvinyl ethers.

In another preferred embodiment, the formulations to be used in

accordance with the invention contain at least perfluorinated and/or partly fluorinated polyethers from group c).

Where polyhydroxy compounds are used in the formulations to be used in accordance with the invention, they are preferably selected from the groups of polyalcohols and carbohydrates and, in one particularly preferred embodiment, from polyhydric alcohols, preferably alkanediols, alkanetriols and most preferably glycerol and the polyethers derived therefrom and also glucose, arabinose, ribulose, fructose and the oligo- and/or polysaccharides derived therefrom and esters and ethers thereof.

The advantage of the use according to the invention and of the chain lubricants according to the invention is that water consumption is significantly reduced. Since the belt lubricating solution is not collected and re-used in the prior art, the process in use today involves an enormous waste of resources. Another advantage is that, providing it is properly applied, hardly any of the formulation drips onto the floor. This results in greater safety and in purely visual advantages in the factory. In addition, soil occurring has sometimes been seen to be repelled by the conveyor belts conditioned with the formulation.

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